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Program Strategies for Standards Development for Hazardous Waste Incineration

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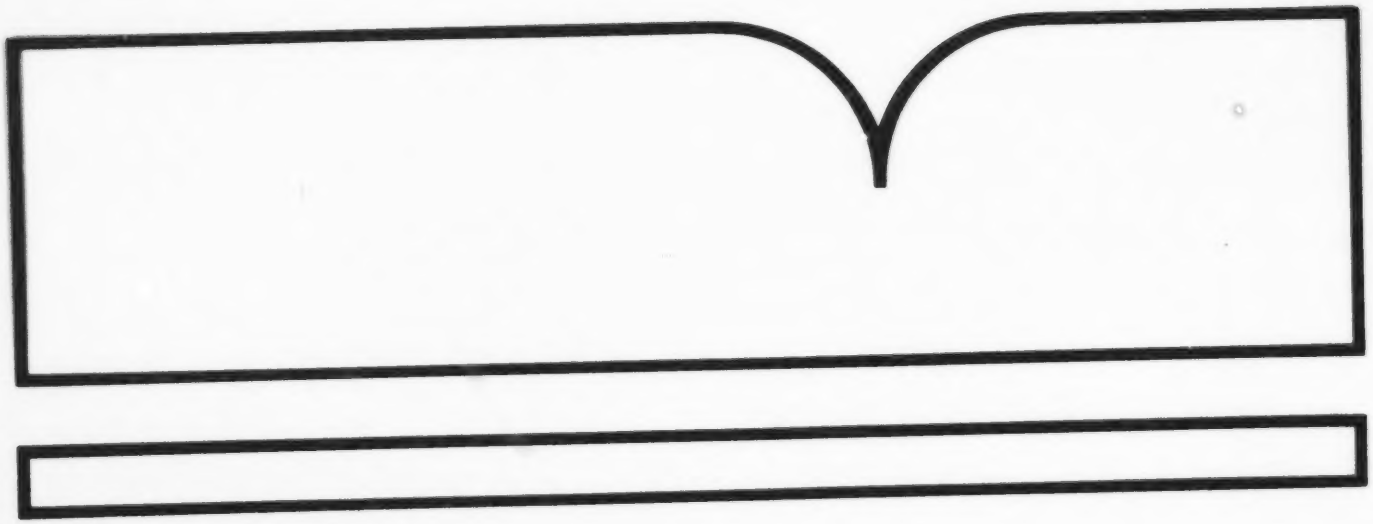

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PROGRAM STRATEGIES FOR STANDARDS DEVELOPMENT FOR HAZARDOUS WASTE INCINERATION

By

Darryl J. von Lehmden

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT

The principal goal of the EPA Environmental Monitoring Systems Laboratory (EMSL) in assessing the quality of measurements is the development of accurate standards that may be used by agency personnel (federal, state, and local) to audit and assess the quality of measurements. EMSL's development of ppb cylinder gas standards, containing hazardous organic compounds, was initiated to meet the need for audit materials to assess the quality of trial-burn-test measurements during hazardous waste incineration. The logic used in selecting organics for this standards development and the procedure used to ensure the highest possible accuracy in these standards are described in this document. Also discussed is the apparent need for high quality gas standards for ambient air hazardous organic measurements and the extent to which the current inventory of 29 organic standards fulfills this need.

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Darryl J. von Lehmden
U. S. Environmental Protection Agency

AUDIT PURPOSE

In the beginning man made measurements. Someone asked, "How good are the measurements?" Then man devised the concept of audits to assess the quality of measurements.

A performance audit is a quantitative assessment of the accuracy of a measurement system. Ideally, a performance audit is conducted during the routine operation of the measurement system and includes an assessment of the precision and the presence of any bias for both the sampling and analysis portions of the measurement system.

EMSL'S GOAL

The principal goal of the EPA Environmental Monitoring Systems Laboratory (EMSL) in assessing the quality of measurements is the development of accurate standards that may be used by agency personnel (federal, state, and local) to audit and assess the quality of measurements. EMSL's development of ppb cylinder gas standards, containing hazardous organic compounds, was initiated to meet the need for audit materials to assess the quality of trial-burn-test measurements during hazardous waste incineration. The logic used in selecting organics for this standards development and the procedure used to ensure the highest possible accuracy in these standards are described in this document. Also discussed is the apparent need for high quality gas standards for ambient air hazardous organic measurements and the extent to which the current inventory of EMSL standards fulfills this need.

SELECTION OF ORGANIC COMPOUNDS FOR STANDARDS

The Resource Conservation and Recovery Act (RCRA)[1] includes performance standards for hazardous waste incineration. One performance standard requires that principal organic hazardous constituents (POHCs) designated in the waste to be incinerated must be destroyed or removed with an efficiency of 99.99 percent or better. POHCs are hazardous waste organic substances in the waste feed that are the most difficult to burn and most abundant. Compliance with this requirement is demonstrated by testing the POHCs in stack emissions and comparing them to the POHCs in the waste during a trial burn test. Facility personnel must successfully demonstrate at least a 99.99 percent destruction removal efficiency (DRE) to obtain an operating permit.

In 1983, EMSL initiated a program to develop ppb cylinder gas standards containing hazardous organic compounds that could be used to audit volatile POHC measurement systems during trial turn tests. On the basis of experience of EPA's Air and Energy Engineering Research Laboratory (AEERL) with RCRA trial burn testing, five organic compounds were selected. The decision was made to place all compounds together so that the same gas standard could be used to audit more than one POHC during a trial burn test. This gas standard, called Group I, is shown in Table 1. The Group I gas standard was initially developed at two concentration ranges to audit the two prevalent test methods for volatile POHCs. The 7 to 90 ppb range standard is used to audit the volatile organic sampling train (VOST), and 90 to 430 ppb range standard is used to audit bag sampling.[2] In early 1984, a study was completed that successfully demonstrated the use of cylinder gas standards in auditing the VOST and bag sampling measurement systems.[3,4] The recommended auditing procedures for the VOST and bag sampling measurement systems are described elsewhere.[3,5]

According to recommendations from AEERL, a nine-compound Group II gas standard was developed in 1984, and a six-compound Group III gas standard was developed in 1985. The Group II and Group III gas standards are shown in Table 1.

In 1986 the six-compound Group IV gas standard was developed (see Table 1). The selection of organic compounds for this gas standard was based on EPA health risk assessment studies plus input from a state agency. As a result of the EPA health risk assessment studies, 1,3-butadiene, ethylene oxide, and methylene chloride have been published in the Federal Register as "Intent-to-List" compounds. This publication means regulatory development efforts are currently under way for each of these air pollutants, but the actual decision to regulate these air pollutants under Section 112, National Emission Standards for Hazardous Air Pollutants (NESHAP) of the Clean Air Act will not be made until the pollutants are published in the Federal Register as "Listed" compounds. EPA has made the decision not to regulate acrylonitrile under Section 112. Instead, this chemical has been referred to selected states for their regulatory consideration. Propylene oxide is currently under health risk assessment by EPA. Ortho-xylene was included in Group IV at the request of a state agency.

After interest was shown in the low ppb gas standards by the ambient air measurement community, development of an 18-compound Group V gas standard was initiated in 1987 (see Table 2). The compounds in this gas standard include 16 of the 27 compounds that are presently in Groups I, II, III, and IV gas standards plus two new compounds, ethyl benzene and 1,2-dichloropropane. The Group V gas standard is intended for auditing ambient air measurement systems and not POHC measurements during RCRA trial burn tests. Therefore, this gas standard is being developed at a low concentration, 1 to 40 ppb, for all organic compounds. The current status of EPA's health risk assessments[6] for compounds in the Group V standard is summarized in the five statements that follow:

1. Benzene is currently a NESHAP for one or more source categories and is a proposed NESHAP for one or more source categories. Also, it is "Listed" (a step prior to regulation proposal) for one or more source categories.

2. Vinyl chloride is currently a NESHAP for one or more source categories. Also, it is "Listed" for one or more source categories.

3. Carbon tetrachloride, chloroform, 1,2-dichloroethane, methylene chloride, 1,3-butadiene, perchloroethylene, and trichloroethylene have been classified "Intent-to-List" (a step prior to "Listed").

4. Ortho-xylene is currently at a point of preliminary health and source screening (a step prior to "Intent-to-List").

5. EPA has made a decision not to regulate toluene and chlorobenzene.

SELECTION OF COMPOUND CONCENTRATIONS FOR STANDARDS

As previously stated, the 7 to 90 ppb and 90 to 430 ppb concentration ranges were selected for the Groups I, II, III, and IV gas standards to audit POHC measurements during RCRA trial burn tests; the lower range standard is used to audit VOST measurements, and the higher range standard is used to audit bag sampling measurements. Later, Groups I and IV standards in the 430 to 10,000 ppb concentration range were added. These standards were added because the RCRA regulation requires a DRE of at least 99.99 percent but does not regulate a maximum emission rate for the POHCs. Therefore, some source testers have received approval to conduct the trial burn test in such a manner that POHC concentrations in stack emissions are about 1000 ppb. This reduces considerably the effect of atmospheric POHC contamination on the VOST measurement system, compared to trial burn tests where the POHC stack emissions are in the order of 10 to 50 ppb concentrations.

The Group V gas standard is intended to audit systems that measure hazardous organic compounds in ambient air. Therefore, this gas standard is being developed at the lowest practical concentrations for all 18 compounds. This gas standard will have organic compounds present in the concentration range of 1 to 40 ppb.

STABILITY OF STANDARDS

To ensure that the concentration of each gas standard remains stable, each standard is periodically analyzed. A two-tier stability assessment is conducted on all gas standards. The first-tier stability assessment is conducted during the preparation of the gas standards by a commercial gas manufacturer. The commercial gas manufacturer on each gas standard must conduct a minimum of two analyses that are separated by at least 30 days. EMSL will accept only those gas standards in which the two analyses agree within 10 to 15 percent depending on the compound. The second-tier stability assessment involves the periodic reanalysis by EMSL (via contract with the Research Triangle Institute in Research Triangle Park, NC) of each gas standard. Once a gas standard is received from the commercial gas manufacturer, it is analyzed as soon as possible, then re-analyzed at 2, 6, and 12 months and annually thereafter. An example of stability data for a Group I ppb gas standard is shown in Table 3. A gas standard is not available for auditing purposes until the 2-month EMSL (Research Triangle Institute) analysis is completed.

TRACEABILITY OF ANALYSES TO NBS

The credibility of a gas standard is no better than the quality of the calibration standards and degree of quality control used during the analyses of the gas standard. EMSL made the decision in 1983 when it initiated the ppb gas standard development program that all analyses must be traceable to National Bureau of Standards (NBS) primary gas standards. Therefore, under an interagency agreement between NBS and EMSL, the NBS has gravimetrically prepared and analytically certified primary gas standards for Groups I, II, III, IV, and V for EMSL for each concentration range shown in Tables 1 and 2. Typically, NBS prepares these primary gas standards simultaneously with the EMSL procurement of commercially prepared mixtures that are used as audit standards. As described elsewhere,[7]

during the stability analyses an NBS primary gas standard is always used for quality control during each analysis day. For Groups III, IV, and V gas standards, separate NBS primary gas standards are also used for calibration. Current plans[7] are to convert all analyses of Groups I, II, III, IV, and V gas standards to cryogenic trapping followed by cryogenic focusing on a gas chromographic column. With this analysis procedure, one NBS primary gas standard will be used for calibration. A second NBS primary gas standard will be used for quality control. A report on the accuracy of the NBS primary gas standards for volatile hazardous organic compounds has been published.[8]

COMPARISON OF ORGANIC COMPOUNDS SELECTED FOR STANDARDS VERSUS THE CURRENT NEED

The true measure of worth of the gas standards is whether they meet the current needs. To address this concern, a comparison has been made by showing four lists of priority air pollutants developed for four distinctly different purposes (see Table 4). The gas standard program was developed initially to meet the growing need to know the quality of volatile POHC measurements during RCRA trial burn tests. Groups I, II, and III compounds were selected with this need in mind. Currently, of the 144 audits that have been initiated using the gas standards, 72 were to assess POHC measurements before or during RCRA trial burn tests. The compounds that were selected for RCRA audits are shown with a letter "A" in Table 4, Column 1. In addition, those Groups I, II, III, and IV compounds that were selected as POHCs for trial burn tests at 23 hazardous waste incinerators[9] are shown with a letter "B" in Column 1.

The compounds currently undergoing EPA health risk assessments[6] or for which these assessments have been completed are shown with a letter "C" in Table 4, Column 2. In addition to the compounds shown, other compounds are included in EPA's health risk assessment studies that are not shown here.

Currently, of the 144 audits that have been initiated, 16 audits were to assess the accuracy of ambient air measurement systems used in conjunction with Superfund hazardous waste sites. The compounds that were selected for Superfund audits are shown with a letter "D" in Table 4, Column 3. The volatile compounds identified in the Superfund Hazardous Substance List (HSL) for analysis in ambient air samples are shown with a letter "E" in Column 3. In addition to the 17 HSL compounds shown, 18 volatile compounds not shown are identified by the EPA Contract Laboratory Program[10] as part of the HSL for volatile compounds.

In 1984 the California legislature passed a bill (AB3525-Calderon) that requires ambient air testing for all active solid waste disposal sites in California. In 1986, the legislature passed a bill (AB3374-Calderon) requiring the California Air Resources Board (CARB) in coordination with the air pollution control districts to publish guidelines for the required testing. Ambient air testing is required at approximately 1000 active solid waste disposal sites. CARB Guidelines[11] cite 10 target compounds for measurement. As shown in Table 4, Column 4, by the letter "F", all 10 of these compounds are contained in the EMSL gas standards.

AVAILABILITY OF STANDARDS

Groups I, II, III, and IV gas standards are currently available for use in conducting audits. The Group V gas standard will be available in October 1987. EPA program and regional offices; federal, state, and local agencies; and contractors performing services for these agencies may obtain the gas standards for audits by contacting:

Robert L. Lampe
U. S. EPA
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, NC 27711
Phone: Commercial 919-541-4531 or FTS 629-4531

Table 1. Currently Available EMSL PPB Gas Standards*

Group I Compounds	Group II Compounds	Group III Compounds	Group IV Compounds
Carbon tetrachloride	Trichloroethylene	Vinylidene chloride	Acrylonitrile
Chloroform	1,2-dichloroethane	1,1,2-trichloro-1,2,2-trifluoro-ethane (F-113)	1,3-Butadiene
Perchloroethylene	1,2-dibromoethane	1,2-dichloro-1,1,2,2-tetra-fluoroethane (F-114)	Ethylene oxide
Vinyl chloride	Acetonitrile	Acetone	Methylene chloride
Benzene	Trichloro-fluoromethane (F-11)	1-4 Dioxane	Propylene oxide
	Dichloro-difluoromethane (F-12)	Toluene	Ortho-xylene
	Bromomethane	Chlorobenzene	
	Methyl ethyl ketone		
	1,1,1-trichloro-ethane		
Group I Ranges	Group II Ranges	Group III Ranges	Group IV Ranges
7 to 90 ppb 90 to 430 ppb 430 to 10,000 ppb	7 to 90 ppb 90 to 430 ppb	7 to 90 ppb 90 to 430 ppb	7 to 90 ppb 430 to 10,000 ppb

*All gas standards are in a balance gas of nitrogen.

Table 2. EMSL Group V PPB Gas Standard Currently Under Development*

Carbon tetrachloride	Methylene chloride
Chloroform	Trichlorofluoromethane (F-11)
Perchloroethylene	Bromomethane
Vinyl chloride	Toluene
Benzene	Chlorobenzene
Trichloroethylene	1,3-Butadiene
1,2-dichloroethane	Ortho-xylene
1,2-dibromoethane	Ethyl benzene
1,1,1-trichloroethane	1,2-dichloropropane

*The Group V range will be 1 to 40 ppb. The balance gas is nitrogen. Group V gas standards will be available in October 1987.

Table 3. Stability of Group I Gas Standard

ACTIVITY		COMPOUND				
		Carbon Tetra-Chloride	Chloroform	Perchloro-ethylene	Benzene	Vinyl Chloride
MANUFACTURER ANALYSIS						
Theoretical	PPB	(9.5)	(39.6)	(9.4)	(18.9)	(20.0)
1st Analysis	Date	11/17/83	11/17/83	11/17/83	12/06/83	12/06/83
	PPB	(7.7)	(42.1)	(9.2)	(15.8)	(18.3)
2nd Analysis	Date	12/16/83	12/16/83	12/16/83	12/15/83	12/15/83
	PPB	(7.1)	(41.2)	(7.7)	(19.6)	(19.2)
RTI ANALYSIS						
1st RTI Analysis	Date	1/06/84	1/06/84	1/06/84	1/23/84	1/23/84
	PPB	(9.3 ±0.3)	(40.0 ±0.8)	(9.4 ±0.2)	(19.6 ±0.6)	(20.2 ±0.6)
2nd RTI Analysis	Day*	59	59	59	49	49
	PPB	(9.3 ±0.3)	(38.7 ±0.8)	(10.3 ±0.2)	(20.0 ±0.6)	(19.0 ±0.6)
3rd RTI Analysis	Day*	238	238	238	226	226
	PPB	(9.5 ±0.3)	(40.6 ±0.9)	(9.5 ±0.2)	(19.4 ±0.6)	(20.6 ±0.7)
4th RTI Analysis	Day*	404	404	404	375	375
	PPB	(9.6 ±0.3)	(37.1 ±0.8)	(9.1 ±0.2)	(19.4 ±0.6)	(20.4 ±0.7)
5th RTI Analysis	Day*					
	PPB	on audit	on audit	on audit	on audit	on audit
6th RTI Analysis	Day*	833	833	833	810	810
	PPB	(10.5 ±0.3)	(40.5 ±0.9)	(11.2 ±0.3)	(19.7 ±0.6)	(19.4 ±0.6)

*Number of days after the first RTI analysis date.

Table 4. Comparisons of Organic Compounds Selected for Standards versus the Current Need.*

Compounds Selected for EMSL Standards	RCRA Trial Burns	Health Risk Assessments	Superfund	California Solid Waste Disposal
Carbon tetrachloride	A-31, B-13	C	D-2, E	F
Chloroform	A-19, B-5	C	D-2, E	F
Perchloroethylene	A-15, B-10	C	D-2, E	F
Vinyl chloride	A-8	C	D-2, E	F
Benzene	A-12, B-3	C	D-3, E	F
Trichloroethylene	A-8, B-8	C	D-3, E	F
1,2-Dichloroethane	A-3	C	D-3, E	F
1,2-Dibromoethane	A-3		D-2	F
Acetonitrile	A-3			
Trichlorofluoromethane (F-11)	A-5, B-1		D-1	
Dichlorodifluoromethane (F-12)	A-3, B-1		D-1	
Bromomethane	A-3		D-1, E	
Methyl ethyl ketone	A-2, B-2		E	
1,1,1-Trichloroethane	A-6, B-6	C	D-3, E	F
Vinylidene chloride	A-1	C	E	
1,1,2-Trichloro-1,2,2-trifluoroethane (F-113)	A-2	C		
1,2-Dichloro-1,1,2,2-tetrafluoroethane (F-114)	A-2			
Acetone	A-1		E	
1,4-Dioxane	A-1			
Toluene	A-4, B-8	C	E	
Chlorobenzene	A-1, B-5	C	E	
Acrylonitrile**		C		
1,3-Butadiene**		C		
Ethylene oxide**		C		
Methylene chloride**	B-5	C	E	F
Propylene oxide**		C		
Ortho-xylene**		C		
Ethyl benzene***			E	
1,2-Dichloropropane***			E	

*Code used in table:
"A" means EMSL standard was used to audit before or during an RCRA trial burn test. The number following "A" is the number of audits with this compound.
"B" means this compound was designated a POHC in a publication suummarizing 23 hazardous waste incinerator trial burn tests.[9] The number following "B" is the number of times this compound was designated a POHC.
"C" means this compound is currently undergoing EPA health risk assessment or the assessment is completed.[6]
"D" means EMSL standard was used to audit either before testing began or at a hazardous waste disposal site. The number following "D" is the number of audits with this compound.
"E" means this compound is on the Superfund Hazardous Substance List[10] of volatile compounds for analysis in ambient air samples.
"F" means this compound is one of 10 target compounds for measurement in ambient air samples collected at all active solid waste disposal sites in California.
**This is a Group IV compound. Group IV standard was not available for audits until June 1987.
***This is a Group V compound. Group V standard will not be available for audits until October 1987.

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